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SYNTHETIC ORGANIC CHEMICALS

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Isotope of Carbon, C^{13}, Now Available

THE Kodak Research Laboratories recently made the first commercial shipment of the stable tracer isotope of carbon, C^{13}, in the 20 to 25 per cent concentration range. Used primarily for the detection of cancer, this material, prepared in the form of potassium cyanide, is being made available by Eastman Kodak Company to the National Research Council's Committee on Growth, acting for the American Cancer Society. Until larger chemical exchange units now under construction are put into operation, only small amounts, at concentrations below 18 per cent C^{13}, will be available for general distribution.

Prices of C^{13} concentrates range from $100 per gram of excess C^{13} at 3 to 5 per cent to $400 per gram at 23 to 26 per cent. As rapidly as possible, synthetic methods will be developed so that certain organic compounds containing C^{13} can also be supplied.

The Research Laboratories also supply ammonium salts and certain organic compounds enriched in N^{15} for tracer purposes. Inquiries regarding either C^{13} or N^{15} should be addressed to Eastman Kodak Company, Research Laboratories, Dept. WOK, Kodak Park Works, Rochester 4, N. Y.

Boron Fluoride Catalysis of Organic Reactions*

By J. ELMORE JONES**

DURING the last fifteen years the use of boron fluoride in place of aluminum chloride and other metal halides for the catalysis of reactions involving condensations, rearrangements, and polymerizations has been studied extensively. Although boron fluoride is generally inferior to aluminum chloride for most of these reactions, it is often used advantageously since reactions catalyzed by it usually do not yield tarry or other undesirable by-products. The smoothness of these reactions is probably due to the small atomic volume and high electron affinity of the boron fluoride molecule, which allows it to form more stable molecular compounds than does aluminum chloride. Boron fluoride catalyzes most successfully those reactions in which water, an alcohol, or an acid is produced, because of its great tendency to form complexes with oxygen-containing compounds.

I. The Synthesis of Esters

Not only boron fluoride but also its complexes with oxygen-containing compounds are excellent catalysts for condensation reactions. The acidity of such compounds as water, alcohols, or acids is increased by complex formation, and this increase in acidity makes boron fluoride a useful catalyst for esterifications. Esters of both aliphatic and benzoic acids are formed easily and in good yields. The esterification of substituted aromatic acids is usually more difficult and requires prolonged refluxing. In these cases the quantity of boron fluoride required for optimum yields depends upon the substituents in the aromatic nucleus. Amino acids require more than one mole of boron fluoride, since the first mole of catalyst forms a complex with the amino group.

A second method of preparing esters involves the addition of an acid to an olefin by the action of boron fluoride. The tendency for olefins to polymerize under the conditions employed limits the usefulness of the reaction, but in certain cases good yields are obtainable. In order to prevent excessive polymerizations of olefins above butylene, the reaction must be carried out at temperatures below 100°C. The addition of the acid to the double bond follows Markownikoff's rule; thus, secondary or tertiary alkyl esters are obtained with olefins above ethylene. Cyclopropane reacts with the production of *n*-propyl esters.

Other compounds, such as amides and nitriles, react with alcohols in the presence of boron fluoride to form esters, but the yields are usually below 50 per cent. A competing reaction when amides are used is the production of a nitrile from two amide molecules.

$$2\ CH_3CONH_2 \xrightarrow{BF_3} CH_3CN + CH_3COOH + NH_3 \cdot BF_3$$

II. Reactions of Unsaturated Compounds

A. ACETYLENE.

As a result of complex formation, a solution of boron fluoride in an alcohol is a strong acid resembling sulfuric acid and will dissolve mercuric oxide. Such a solution containing the oxide is an excellent medium for converting acetylenic compounds into acetals. The catalyst is actually the mercuric salt of the boron fluoride alcoholate.

$$HC{\equiv}CH + CH_3OH \xrightarrow{Hg(OCH_3 \cdot BF_3)_2} CH_3CH(OCH_3)_2$$

This method has the advantage of pro-

*This article is a condensation of a chapter on "Boron Fluoride as a Catalyst in Chemical Reactions" by D. Kastner in the book, "Newer Methods of Preparative Organic Chemistry," by Interscience Publishers, Inc., New York, 1947.

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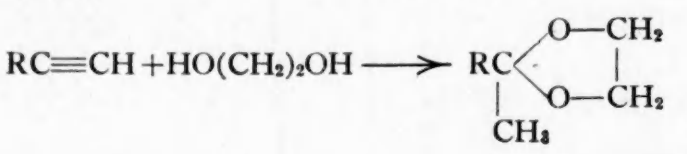
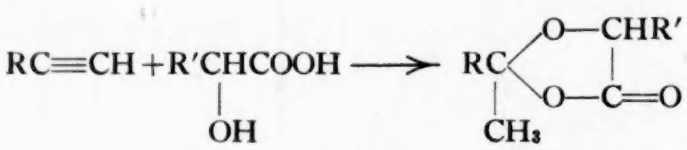
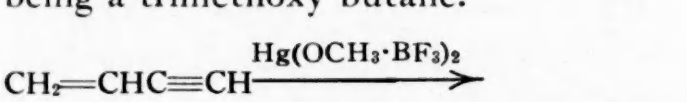
ducing fewer by-products than does the one with sulfuric acid. It also makes available acetals, such as those of benzyl alcohol not easily obtainable by any other method. Aliphatic polyhydroxy compounds react with acetylene to give excellent yields of cyclic acetals.

Methanol is the only monohydric alcohol which forms ketals from substituted acetylenes, since the other alcohols give polymeric products. On the other hand, polyhydric alcohols and α-hydroxy acids form cyclic products with alkyl acetylenes.

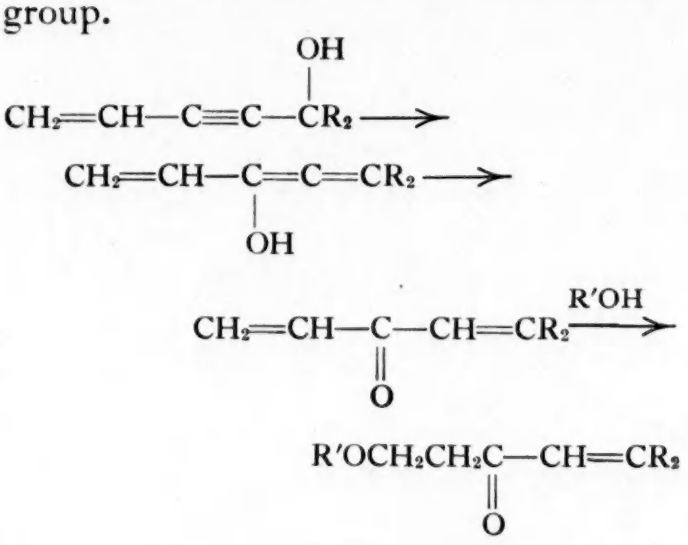




The conjugation of the double bond with the triple bond in vinyl acetylene makes it capable of adding methanol also, the product from such a reaction being a trimethoxy butane.

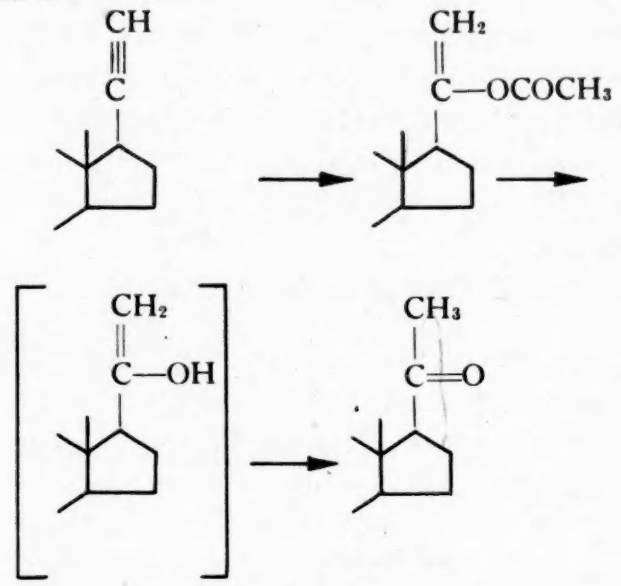


In the case of secondary or tertiary vinyl ethynyl carbinols, the reaction has been shown to involve a rearrangement of the carbinol with subsequent addition of alcohol to the unsubstituted vinyl group.



The condensation is complete in three to four hours at 25°C. and yields as high as 77 per cent have been obtained.

The addition of an organic acid to an acetylenic compound follows a course similar to that of an alcohol. The products are vinyl (enol) esters. The reaction has been applied by Ruzicka in the preparation of the 17-methyl ketones of certain steroids and sex hormones. The 17-ethynyl derivatives were converted to the enol esters by the action of boron fluoride and mercuric oxide in acetic acid anhydride solution. Subsequently, the acetates were hydrolyzed.



B. POLYMERIZATION OF OLEFINS.

The polymerization of olefins has recently been used extensively in the manufacture of liquid fuels, lubricating oils, synthetic polymers, and intermediates for use in other condensation reactions. Although boron fluoride affects many of these reactions, it has not been employed commercially to any great extent because of its high cost and complications involved in its recovery. Olefins, such as propylene, butadiene, and styrene, have a greater tendency toward polymerization, with increasing substitution on either of the doubly bound carbon atoms.

The viscosities of the oils resulting from the polymerization of the gaseous olefins depend upon the conditions of pressure and temperature used. The viscosities increase as the temperature is lowered, particularly with isobutylene, and at −80°C. products having molecular weights in excess of 200,000 are ob-

tained. The rate of reaction is increased markedly by the presence of a little hydrogen fluoride, water, or finely divided nickel.

The polymerization reactions mentioned, in which boron fluoride alone is the catalyst, are comparable to those in which aluminum chloride is used. A second type which involves boron fluoride complexes resembles those catalyzed by phosphoric acid. This type is usually carried out under pressure at temperatures above 100°C. When boron fluoride dihydrate is used, the reaction mechanism appears to be similar to that involved in phosphoric acid catalysis; the catalyst adds to the olefin to produce the boron fluoride dialcoholate which then reacts with a second molecule of the olefin.

Rubber in solution in benzene or carbon tetrachloride is cyclized by 4 to 7 per cent of boron fluoride in acetic acid in three hours or less. The products, depending upon the extent of reaction, vary from easily torn masses to solid leatherlike polymers. They still contain double bonds and can be vulcanized to produce substances which can be used for coating materials and for insulation. The polymerization of cumarone oil and resin acids gives products with similar properties.

Other compounds which are useful for catalyzing the polymerization of indene, styrene, cumarone, phenylbutadiene, and isoprene are phenyldiazonium borofluoride, $C_6H_5N_2BF_4$, and the tetrazonium borofluoride, $C_6H_4(N_2BF_4)_2$. Turpentine and olefins from cracked paraffins produce oils and resins useful for varnishes.

(*Continued in next issue*)

New Eastman Organic Chemicals

2037	Acrolein (Stabilized with Hydroquinone) BP 51-53° CH_2:CHCHO...MW 56.06	100 g.	$1.80 C
5808	2-Amino-5-diethylaminopentane BP 70-72°/6mm $(C_2H_5)_2NCH_2CH_2CH_2CHNH_2CH_3$...MW 158.28	100 g.	7.00 C
5798	p-Aminopropiophenone MP 141-143° $NH_2C_6H_4COCH_2CH_3$...MW 149.19	100 g.	3.50 C
P 5800	2-Bromo-5-diethylaminopentane Hydrobromide (Pract.) $(C_2H_5)_2NCH_2CH_2CH_2CHBrCH_3 \cdot HBr$...MW 303.10	100 g.	7.50 C
2571	α,β-Dibromobutyric Acid MP 86-87.5° $CH_3CHBrCHBrCOOH$...MW 245.92	100 g.	6.00 C
P 5788	2,4-Dichlorobenzoyl Chloride (Pract.) MP 15-18° $Cl_2C_6H_3COCl$...MW 209.47	500 g.	3.00 D
P 5789	2,4-Dichlorotoluene (Pract.) BP 198-200° $Cl_2C_6H_3CH_3$...MW 161.03	1 kg.	3.70 E
5809	1-Diethylamino-4-pentanol BP 84-86°/6mm $(C_2H_5)_2NCH_2CH_2CH_2CHOHCH_3$...MW 159.27	100 g.	7.00 C
5793	5,5-Diphenylhydantoin MP 293-295° $NHCONHCOC(C_6H_5)_2$...MW 252.26	100 g.	2.50 C
3076	Malononitrile MP 30-32° $CNCH_2CN$...MW 66.06	10 g.	1.75 C
P 5801	Methyl α-hydroxy-iso-butyrate (Pract.) 90% boiling at 134-137° $(CH_3)_2COHCOOCH_3$...MW 118.13	1 kg.	3.15 G
5822	Sorbic Acid MP 134-136° CH_3CH:CHCH:CHCOOH...MW 112.12	500 g.	5.00 D